Measurement of Entrained Organic Droplet Sizes and Total Concentration for Aqueous Streams from the Caustic-Side Solvent Extraction Process

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ABSTRACT

The Modular Caustic-Side Solvent Extraction Unit (MCU) and the Salt Waste Processing Facility will remove radioactive cesium from Savannah River Site supernate wastes using an organic solvent system. Both designs include decanters and coalescers to reduce carryover of organic solvent droplets. Savannah River National Laboratory personnel conducted experimental demonstrations using a series of four 2-cm centrifugal contactors. They also examined organic carryover during operation of a CINC (Costner Industries Nevada Corporation) V-5 contactor under prototypical conditions covering the range of expected MCU operation. This report details the findings from those studies and the implications on design for the MCU.

Key Words: Solvent extraction, Organic carryover, Contactor

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INTRODUCTION

The Modular Caustic-Side Solvent Extraction Unit (MCU) and the Salt Waste Processing Facility will remove radioactive cesium from Savannah River Site supernate wastes using organic solvent extraction system. Carryover of the paraffinic (Isopar® L – based) solvent presents concerns for facilities downstream of these solvent extraction processes. Downstream processes include Saltstone grouting of the low-cesium stream and vitrification of the high cesium strip stream. This work operated 2-cm contactors for both Strip (Defense Waste Processing Facility) and Extraction (Saltstone) simulated streams and a Costner Industries Nevada Corporation (CINC) V-5 contactor for a simulated strip stream only. The carryover of concern consisted of organic droplets dispersed in the aqueous phase, the droplets typically being less than 20 microns in diameter. Droplets and organic concentrations were characterized by turbidity measurements, Microtrac® particle size analysis, optical microscopy, and organic extraction followed by gas chromatography and mass spectroscopy.

The primary goals of this work were to complete characterization of contactor-produced aqueous outputs so that organic concentrations and methods of organic concentration reduction could be evaluated. Past work at Savannah River National Laboratory measured organic carryover during CSSX flowsheet demonstrations with 2-cm centrifugal contactors and actual tank waste.[1,2,3,4] Subsequently, Argonne National Laboratory (ANL) used 4-cm centrifugal contactors and simulated solutions to study the effects of contactor conditions on organic carryover.[5,6] A summary of results for strip solution and decontaminated salt solution (DSS) is in Table 1.

The ANL-02/34 4-cm contactor study found inconsistencies in the organic analyses leading to the large range of values shown in the table. Analyses based on the BoBCalix[7] cesium extractant, organic Cs-7SB[8] modifier additive, and Isopar® L were noted to be inconsistent. Much of the inconsistency at that time was ascribed to possible evaporation of Isopar® L from the samples.

EXPERIMENTAL

Process Fluids

The high-sodium fluid used to simulate DSS had the composition shown in Table 2. It represents an average tank waste composition at SRS and has a density of 1.25 g/mL.

Aqueous strip solution was deionized water with nitric acid added to a concentration of 0.001 M (pH =3).

Typical process solvent was used in this work. It consisted of 69.2 wt% Isopar® L, 29.6 wt % Cs7SB modifier (0.75 M), and balance being BoBCalix (0.007 M) and trioctylamine (0.003 M).

Contactor Operations

Testing used a CINC V-5 centrifugal contactor (i.e., plant-typical size) along with a bank of four 2-cm contactors in a separate setup. The CINC V-5 contactor had a 2.45 inch aqueous weir plate installed. This was appropriate for stripping operations. All materials contacting the MCU solvent were limited to glass, stainless steel, and Teflon® to avoid contamination of the solvent by leaching of plasticizers from plastic materials. Figure 1 shows the equipment.

A bank of ANL 2-cm centrifugal contactors,[9] was set up in a chemical hood along with glass decanters. Figure 2 is a photograph of the equipment and Figure 3 is a diagram of the flows. To improve stage efficiency, the hole at the bottom of each rotor was modified to make the rotor partially pumping.[10] Bottom holes were all 0.42 inches in diameter. Motor shafts were extended from previous designs to allow visual verification of rotation.[11] All contactors in this work used aqueous weirs designed for strip operation. The aqueous weirs had a diameter of 0.481 to 0.482 inch.

Glass decanters similar to those used in reference 17 were used for these experiments. Decanters D-1 or D-3 for aqueous streams had sidearms to deliver decanted product. They also had separate sidearms with stopcocks for removal of organic solvent layers that would be captured in the decanter. The organic decanter D-2 had an internal underflow weir and a sidearm for delivery of decanted organic solvent. It had a bottom drain with stopcock for removal of any aqueous phase that settled out.

Analytical Methods

Quantification of minimum organic droplet size, the droplet size distribution, and the total organic content from the aqueous strip and salt waste streams required advancement of analytical techniques. Results are summarized in the following sections.

Particle Size Distribution for Droplet Size

Successful designs of some organic removal options for aqueous streams depend upon accurate knowledge of organic droplet size. Design of coalescers and centrifuges are examples. The Analytical Development Section performed initial work on microscopic glass beads with a Microtrac® S3000, discovering that the instrument would likely succeed with the similar transparent system of organic droplets in aqueous phases.[12] The instrument requires particle-free, pre-filtered liquid matrix (300 mL per sample), estimates of liquid and transparent bead indices of refraction, and selection of the "transparent" system option. The current work used the Microtrac® S3000 supported by optical microscopy to verify results.

Sample age for this analysis was considered especially important because the larger organic droplets rise to the top of samples and coalesce with time. Aqueous strip solution samples were analyzed at a target time of 2 hours after sampling commencement, this being less than the 500-minute residence time for the MCU strip decanter. Simulated DSS samples were analyzed one hour after sampling commencement, this also being shorter than the 170-minute residence time for the MCU DSS decanter. The goal was to remove the readily-decanted second phase so that this work could focus on the more troublesome and persistent organic dispersion.

While the work used a specific procedure for operation of the Microtrac® S3000,[13] a general list of steps is given here:

1. The instrument (S3000 with separate circulating control unit) is charged with approximately 300 mL of matrix-matched filtered aqueous liquid after routine flushing of the machine are performed.
2. The S3000 provides a baseline reading of particles in the liquid. The count rate must be less than a machine-determined limit to indicate that the instrument and fluid are clean and free of air bubbles.

3. Normally a few mL of sample is introduced into the circulating stream. Particles in the sample will immediately boost the count rate. Further sample is added to adjust the count rate to a new level specified by S3000 operating procedure.
4. Number-weighted count scans are recorded and averaged.
5. The S3000 calculates volume-weighted particle distribution from the number-weighted data.
6. Results for the sample are printed in the form of tabulated percentages of particles less than machine-established bin sizes, along with a bar graph of the levels in each bin.

Optical Microscopy

Optical microscopy was included in this work because the Microtrac® S3000 was recognized to have a major limitation: it does not distinguish between spherical organic droplets and foreign non-spherical particles. Optical micrographs readily identify whether organic droplets are actually present in an aqueous phase. They also provide general estimates of droplet size. The micrographs allow identification of precipitates, air bubbles, or other foreign materials if present. Organic droplets are identified by their round, transparent, and refractive appearance. Air bubbles, while round, appear very dark because of their much lower refractive index relative to aqueous liquid phases. Foreign materials would be identified primarily by non-spherical shapes.

Samples were analyzed optically at the same time that Microtrac® portions of the same samples were examined, using a Zeiss Axiovert™ 100A metallograph. Low reflectivity of the samples resulted in very little contrast in the images. Use of Differential Interference Contrast (DIC) and Normarksi lighting techniques were employed. Samples were placed on thin microscope slides. Cover slides were used when they were found to improve imaging of droplets.

Organic content

Semi-volatile organic analysis (SVOA) by gas chromatography-mass spectroscopy (GC-MS) quantified Isopar® L concentration in aqueous dispersion samples. Determination of the Isopar® L component was considered paramount because (1) it is the major component of the solvent, and (2) it is the only component that provides a credible flammability concern because

of its flash point of approximately 62 ºC in the pure state. The cesium-extracting components BoBCalix, Cs-7SB modifier, and trioctylamine (TOA) are much less volatile by comparison. In addition the BoBCalix and TOA are present in the solvent at concentrations of 0.007 M or less. TOA is semivolatile and can be determined by SVOA GC-MS methods, but is nevertheless a minor component of the solvent mixture.

SRNL Personnel sealed samples of organic solvent dispersed in aqueous solutions in glass vials with Teflon® lined caps to avoid evaporation of the volatile organic. Personnel filled the vials nearly full to minimize losses to the vapor space of the vials.

Aqueous GC-MS samples were extracted using methylene chloride by the following general steps. All of the sample was placed in a separatory funnel after weighing the sample in its vial. Three sub-portions of methylene chloride were applied in sequence to the sample vial and cap to ensure the capture of all organic in the sample as submitted. The ratio of sample volume to total methylene chloride volume was 3:1. The clean sample vial and cap were weighed to allow determination of sample mass. Personnel contacted each sub-portion of methylene chloride with the sample itself in the separatory funnel. The three methylene chloride extracts were collected in one container and concentrated by nitrogen evaporation at room temperature.

The concentrated methylene chloride extract was analyzed by GC-MS. Analytical separations occurred on an Agilent 6890 gas chromatograph equipped with a 30 m DB-XLB column. The column had a diameter of 0.18 mm and a film thickness of 0.18 micron. Quantification used an Agilent 5973 mass selective detector. Personnel confirmed the mass spectrometer tuning within 24 hours prior to each measurement using perfluorotributylamine. The accuracy claimed for the Isopar® L determinations – based on standards – is ±10%. Analyses focused primarily on Isopar® L content – i.e., the flammable organic constituent – but personnel also analyzed selected samples for TOA and modifier.

Turbidity

Turbidity measurements during contactor operations helped determine steady state. Personnel also measured turbidity at times concurrent to those of the Microtrac® and metallograph (microscope) analyses. An Orbeco-Hellige Model 965 turbidimeter was employed.

RESULTS

Organic Dispersion Characterization

Microtrac® performance and optical microscopy both worked well in obtaining credible drop size distributions with the optical verification that micron-sized organic drops were indeed being measured. Figures 4 and 5 below are examples from the same sample. A 500 X magnification was typically achievable, with 1000 X magnification sometimes providing a useful picture. No droplets below 0.5 micron were detected in strip solutions.

Turbidity

Figure 6 compares turbidity data from SE with reported mass concentrations of Isopar® L. The linear fit includes the origin because pure water has no turbidity. The data do appear roughly linear though two outlier points are present. This positive trend between turbidity and organic content would be expected since a higher concentration of organic droplets would increase the scattering of light.

Investigations of Methods to Clarify the Dispersions

Glass Fiber Filter

Slow gravity flow of strip solution with dispersed solvent from the 2-cm contactor bank was passed by slow gravity flow through a fiberglass filter. This work used a Millipore™ Glass Fiber Prefilter, catalog number APFF09050, rated at 0.7 micron. The filter material was made of very fine glass fiber and was approximately ¾ mm thick. Figure 7 shows the significant difference in clarity – the hazy sample on the left was not filtered, and the product on the right had passed through the filter medium. Slow manual addition limited the pressure driving force through the filter to less than 0.25 inch of water column at all times. The filter pad shown produced about 1 mL/min of clarified liquid under this condition. This result suggests that coalescers, properly designed, can significantly reduce organic carryover to downstream processes.

Organic Concentration for Caustic-Side Solvent Extraction

Coalescer Downstream of the V-5

The experiment produced fresh DSS/organic dispersion from the contactors for testing of a small stack of "Teflon® Fiber Interceptor-Pak™" elements from ACS Separations, Inc. The stack was about two inches long. The work noted a small reduction in organic, though it is unclear whether the coalescer stack was the primary cause of this. Sample handling and exposure to new equipment may have also removed some material. Coalescer stack performance appeared mediocre in this test. Turbidity increased, possibly caused by fines contributed by the coalescer elements. A small but not thorough flush of the stack elements had been performed before the test. Some dark fines similar in color to the Teflon® elements were noticed in handling and using the coalescer material.

CONCLUSIONS

Initial work with contactors provided organic carryover data from a 2-cm centrifugal contactor bank. The following observations are noted.

- Organic carryover values were within the ranges of those found in prior work. The experiment found that organic carryover after decanting was bounded by 417 ppm_m of Isopar® L for the strip/organic tests. Carryover did not exceed 88 ppm_m of Isopar® L for solvent contacted with DSS simulant. Concentrations of total organic from the CINC V-5 contactor discharge, based upon modifier measurements, in the acid typically averaged 330 ppm_m, for a range to 190 – 610 ppm_m.
- No organic droplets greater than 18 micron were detected in any of the work. Strip output contained droplets down to 0.5 micron in diameter. Droplets of solvent in DSS were almost monodisperse by comparison, having a size range 4.7 +/- 1.6 micron in one experiment and 5.2 +/- 0.8 micron in the second sample. This work never found the 100-200 micron size particles reported in ANL work.
- Process throughputs and planned operating conditions result in very stable hydraulics, suggesting that the MCU stripping stages will have spare operating capacity.
- A 0.7 micron fiberglass filter provided significant removal of dispersed organic phase from strip solution.

- Scouting tests with a vendor coalescer material downstream of the V-5 promoted coalescence of smaller size droplets from the decanter effluent but thickness must be significantly larger than those tested here to achieve process-significant organic removal.
- The V-5 contactors operated with relatively cool surfaces under the planned operating conditions.
- This study developed and demonstrated the effectiveness of several analytical methods for support of the Caustic-Side Solvent Extraction process including infrared spectroscopy and droplet size measurement by a MicroTrac® S3000.

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[7] BOBCalixC6 is an acronym for Calix[4]arene-bis(*tert*-octylbenzo-crown-6)

[8] Modifier, or Cs-7SB, are acronyms for (1-2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, CAS #308362-88-1

[9] D. D. Walker, et al., WSRC-TR-2001-00223, April 19, 2001.

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[11] D. D. Walker, et al., WSRC-TR-2001-00223, April 19, 2001.

[12] C. A. Nash, W. D. King, "Preliminary Investigation of CSSX Organic Solvent Drop Size," SRNL-LWP-2005-00006, January 19, 2005.

[13] Manual L16.1 Procedure ADS-1119, "Procedure for Operating the Microtrac S3000 Particle Size Analyzer (U)," Rev. 0, Effective Date: July 15, 2003.

Table 1. Summary of Organic Entrainment Measurements

Report documenting Campaign	Type of Aqueous Output	Organic Content from Aqueous Decanter expressed as ppm by volume
WSRC-TR-2001-00372	DSS	350 in final 12 hours
	Strip	Less than 6
WSRC-TR-2002-00243, rev. 1	DSS	190 on average
	Strip	20 to 320
WSRC-TR-2002-00307	DSS	170
	Strip	510
ANL-02/08	DSS	120 to 241
	Strip	4 to 125
ANL-02/34	DSS	3 to 300

Table 2. Formulation of DSS Simulant

Component	Target Molarity	Measured Molarity
Free hydroxide	1.33	
Nitrate	2.60	
Aluminum (as aluminate)	0.429	0.41
Nitrite	0.134	
Sulfate	0.521	0.51
Carbonate	0.026	
Total Sodium	5.60	5.4

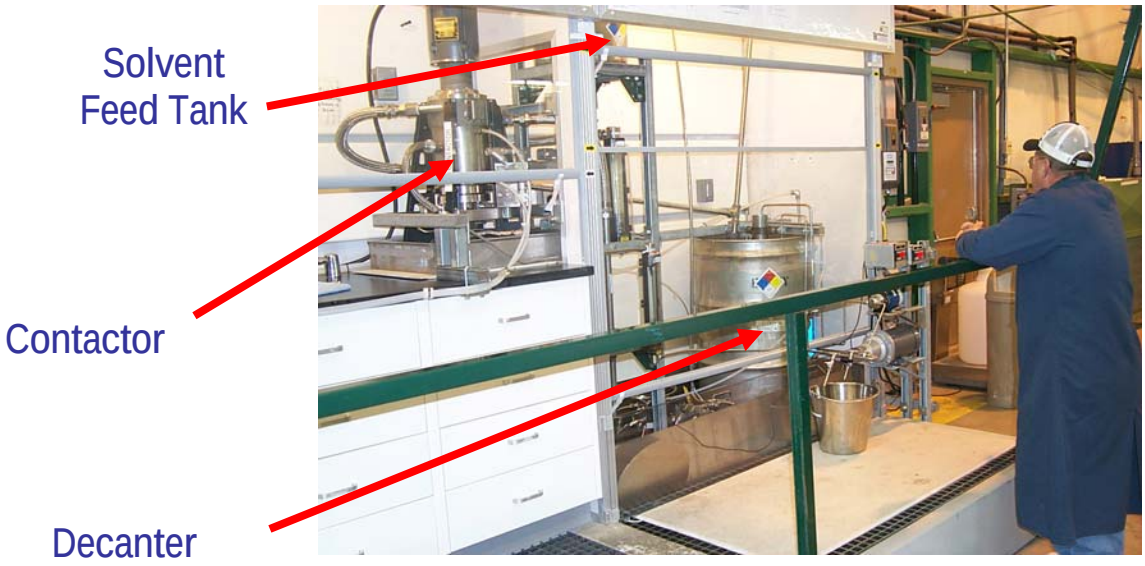

Figure 1

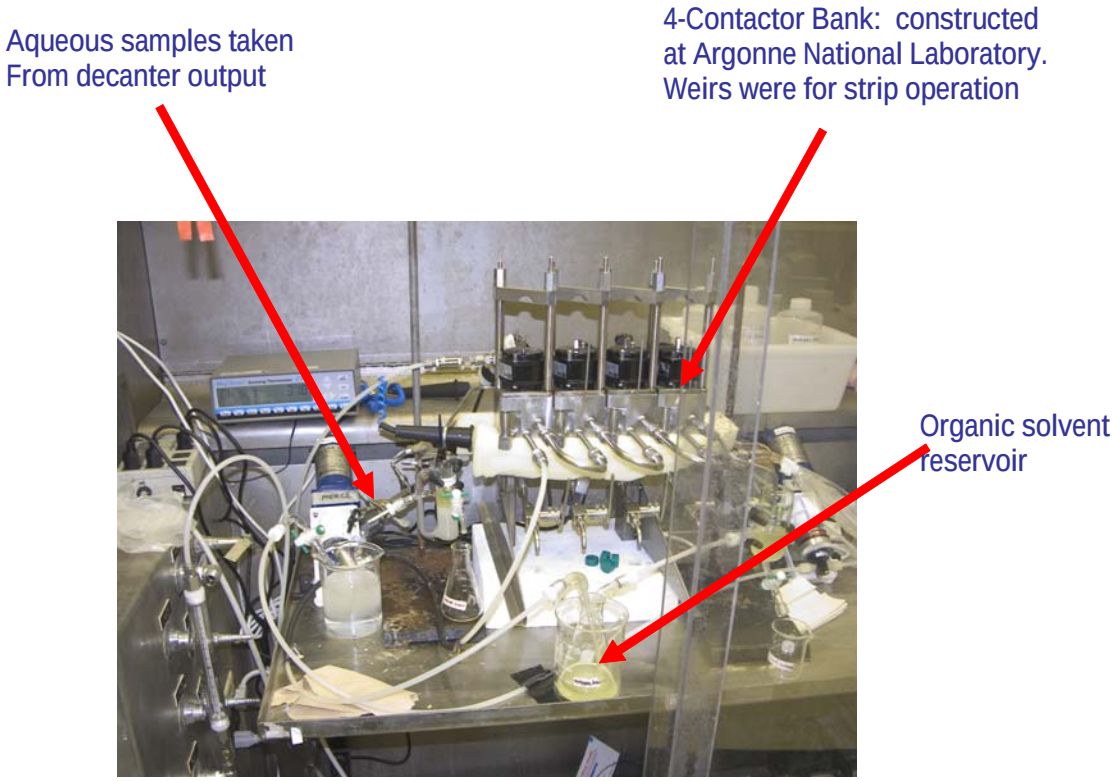

Figure 2

Organic Concentration for Caustic-Side Solvent Extraction

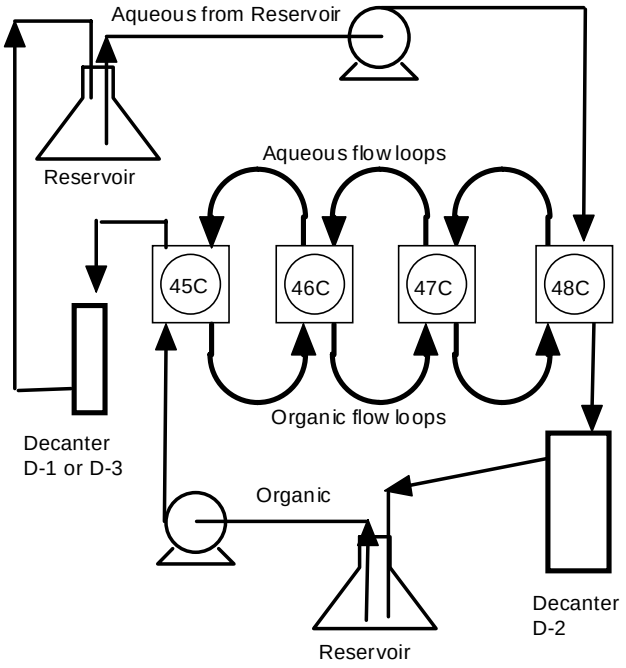

Figure 3

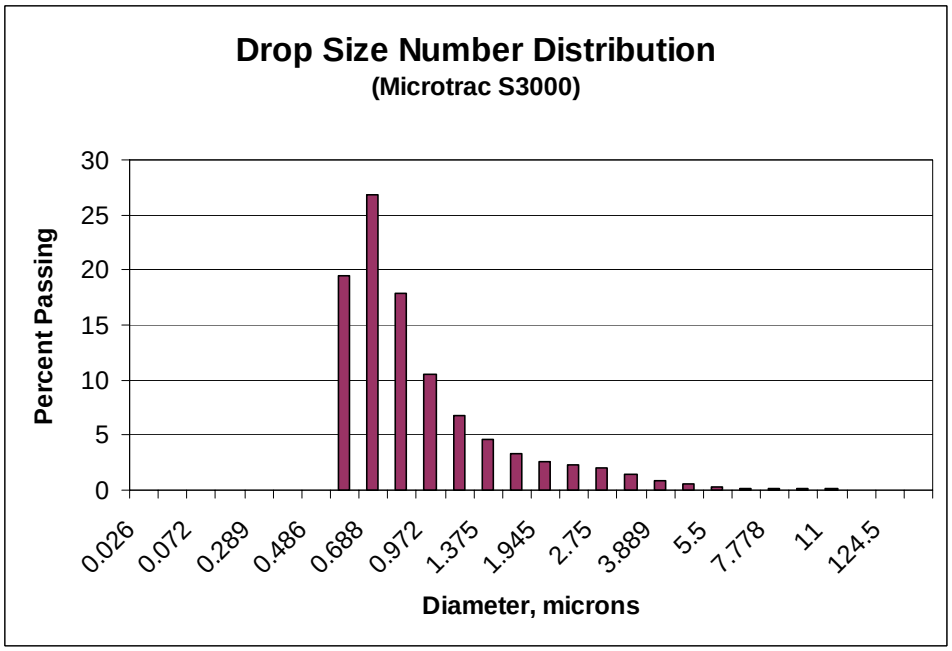

Figure 4

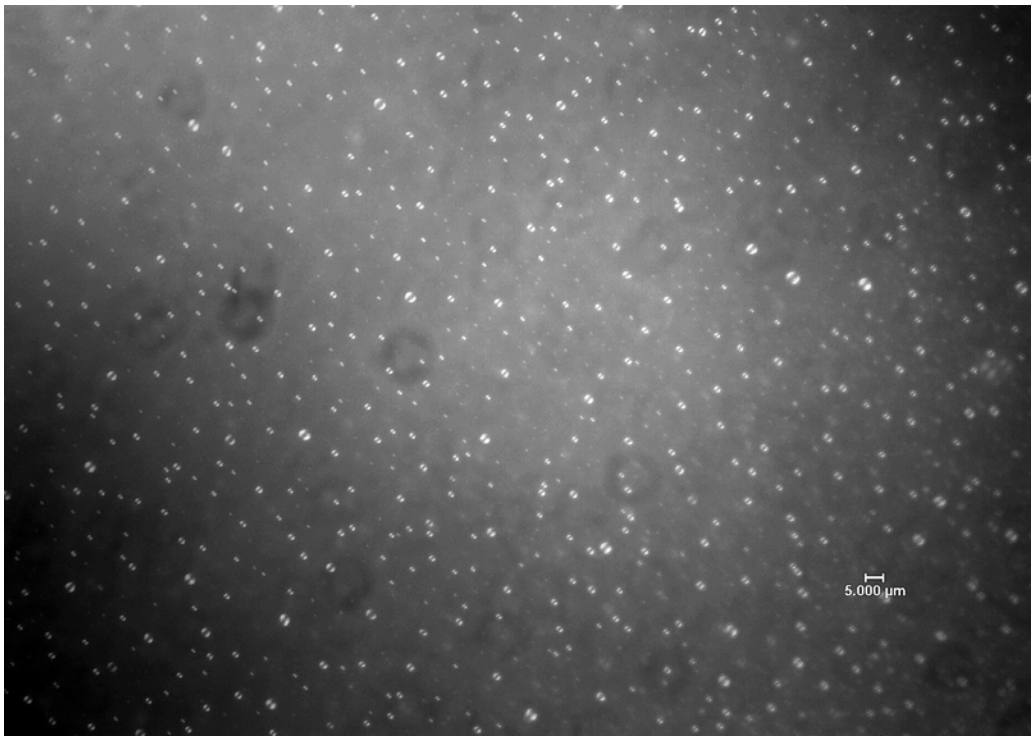

Figure 5

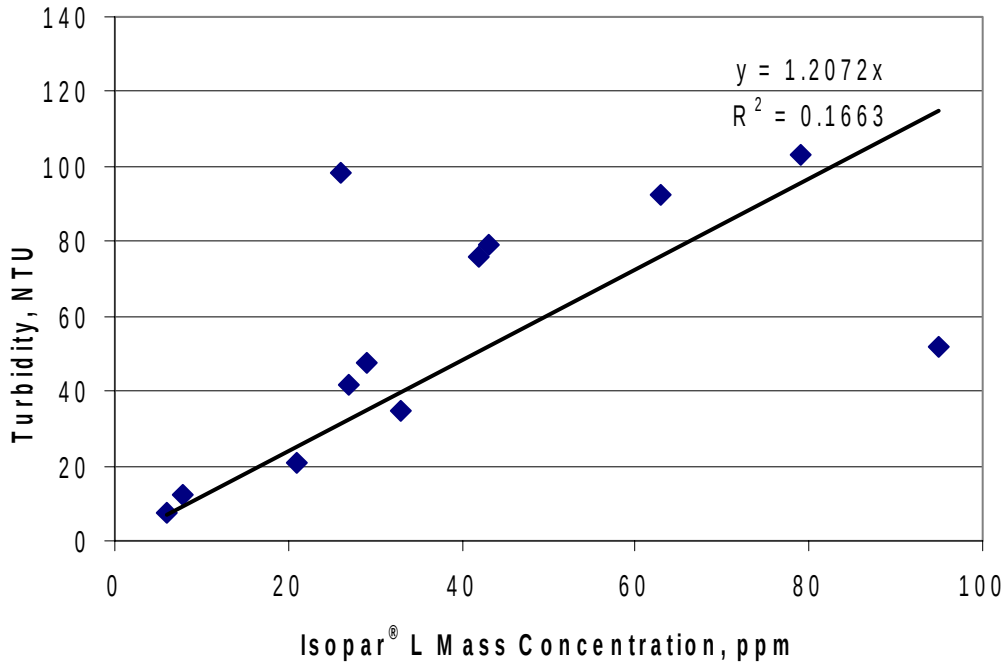

Figure 6

Figure 7